

Effects of Ensembles on Methane Hydrate Nucleation Kinetics

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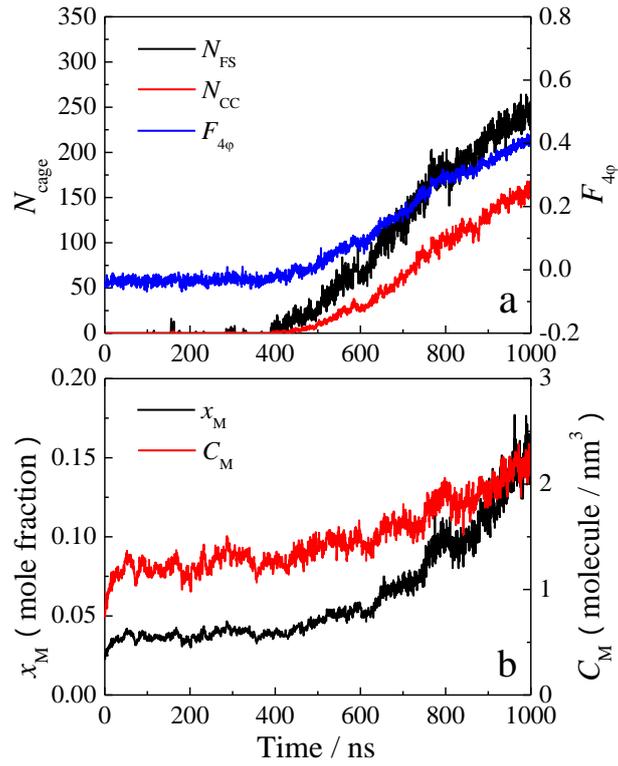


Fig. S1. The time evolution of order parameters, including numbers of cages (N_{FS} and N_{CC}), $F_{4\phi}$, and methane concentration (x_{M} and C_{M}) in liquid solution for the typical NVT trajectory. Here, $x_{\text{M}} = N_{\text{M-dissolved}} / (N_{\text{M-dissolved}} + N_{\text{W-total}} - N_{\text{W-hydrate}})$ and $C_{\text{M}} = N_{\text{M-dissolved}} / (V_{\text{total}} - V_{\text{bubble}} - V_{\text{hydrate}})$, where $N_{\text{M-dissolved}} = N_{\text{M-total}} - N_{\text{M-gaseous}} - N_{\text{M-guest}}$, and hydrate phase is identified when a hydrate nucleus exceeds the critical size of 17 FS-cages.

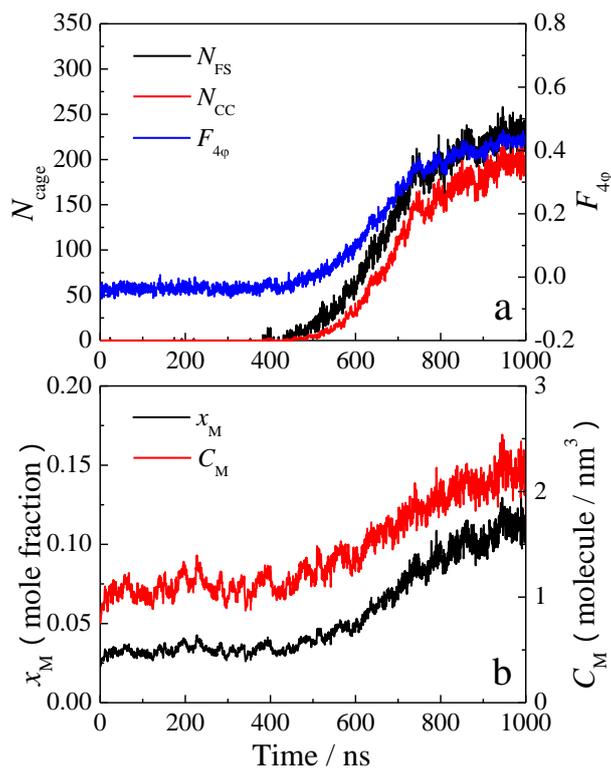


Fig. S2. The time evolution of order parameters, including numbers of cages (N_{FS} and N_{CC}), $F_{4\phi}$, and methane concentration (x_{M} and C_{M}) in liquid solution for the typical *NVE* trajectory. Here, $x_{\text{M}} = N_{\text{M-dissolved}} / (N_{\text{M-dissolved}} + N_{\text{W-total}} - N_{\text{W-hydrate}})$ and $C_{\text{M}} = N_{\text{M-dissolved}} / (V_{\text{total}} - V_{\text{bubble}} - V_{\text{hydrate}})$, where $N_{\text{M-dissolved}} = N_{\text{M-total}} - N_{\text{M-gaseous}} - N_{\text{M-guest}}$, and hydrate phase is identified when a hydrate nucleus exceeds the critical size of 13 FS-cages.

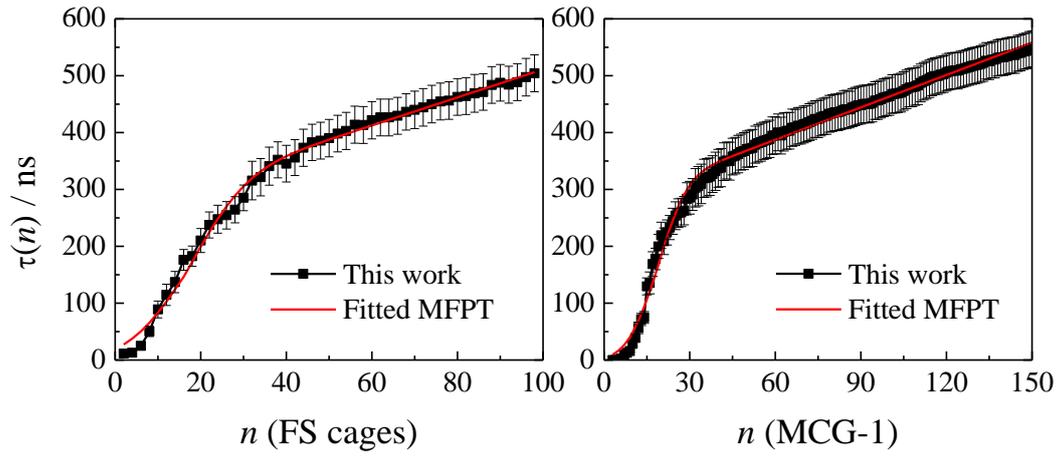


Fig. S3. Mean first-passage time as a function of the largest cluster size (number of the FS cages or the MCG-1 value, n) for the *NVT* ensemble.

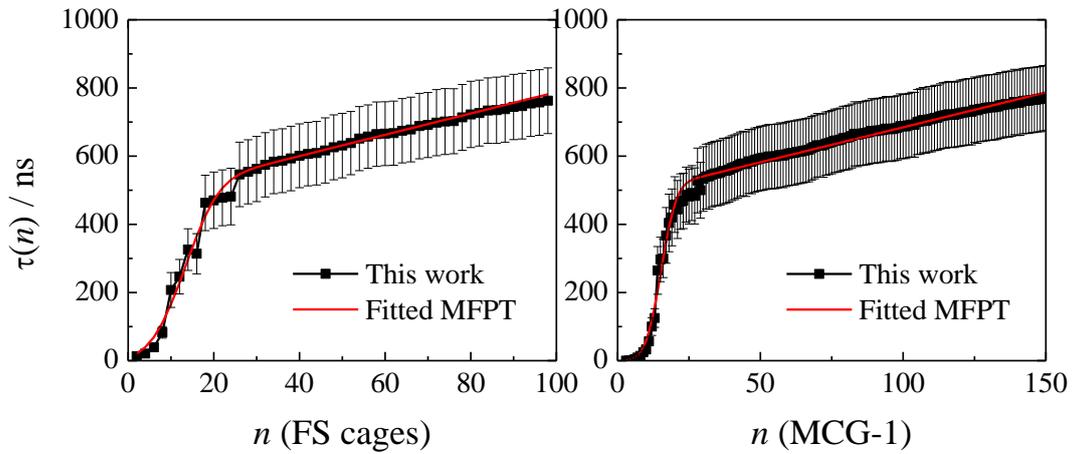


Fig. S4. Mean first-passage time as a function of the largest cluster size (number of the FS cages or the MCG-1 value, n) for the *NVE* ensemble.

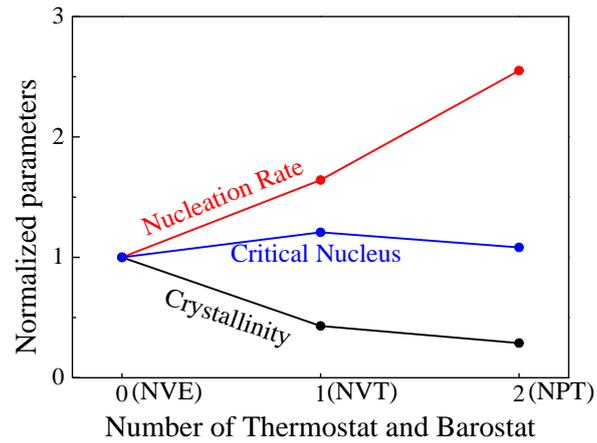


Fig. S5. The trends of nucleation rate, critical nucleus, and crystallinity for the *NPT*, *NVT*, and *NVE* ensembles. The horizontal axis shows the number of thermostat and barostat used for each ensemble. The vertical axis shows the parameters normalized by that of the *NVE* ensemble, respectively. This figure shows the results for the MCG-1 OP in Table 1.